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An EPR spectrometer was purchase with funds obtained with DURIP grant N00014-998-0448. This instrument, which has been operational since November 1998, has been used to characterized structure/functional properties of new materials. These materials are used for gas storage/release and transport, sensors and catalysis. Materials that rapidly and reversibly bind O <sub>2</sub> and NO have been fabricated. Biomedical applications include artery (smooth muscle) relaxation under biologically relevant conditions which is induced by the release of NO from an NO-containing polymer. Platelet formation is also inhibited by this NO-releasing material.				
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## FINAL REPORT

Grant #: N00014-98-1-0448, Mod A00001

PRINCIPAL INVESTIGATOR: A. S. Borovik

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GRANT TITLE: EPR Spectrometer for Probing Biomimetic Metal Sites

REPORTING PERIOD: 02 March 1998 - 02 February 1999

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OBJECTIVE: To obtain an EPR spectrometer that will be used to characterize new materials funded under ONR project N00014-96-1216. In addition, this instrument will be used to teach graduate students and postdoctoral associates fundamental aspects of EPR spectroscopy.

APPROACH: Novel materials are designed and fabricated by template copolymerization methods to mimic metalloproteins. Defined templates containing metal ions are used to form immobilized metal sites in synthetic porous organic hosts. Structural homogeneity of the immobilized sites are ensured by the use of inert metal-complex. The immobilized sites are insulated from one another which prohibits intermolecular degradation pathways. EPR spectroscopy is utilized in the characterization of immobilized sites in these new materials.

ACCOMPLISHMENTS: We have designed and synthesized a series of new materials that have immobilized metal sites in porous hosts. These materials have tunable stereo-electronic properties that have been applied to gas storage/release and transport, sensors and catalysis. Materials that rapidly and reversibly bind O<sub>2</sub> and NO have been fabricated. Pronounced spectroscopic changes are observed for these materials upon gas binding/dissociation. Biomedical applications include artery (smooth muscle) relaxation under biologically relevant conditions which is induced by the release of NO from an NO-containing polymer. Platelet formation is also inhibited by this NO-releasing material.

EPR measurements that were made possible with the instrument obtained with this grant have been critical in determining the structural and functional properties of these materials. The EPR spectrometer arrived in early November 1998 and has

been operational since 15<sup>th</sup> November 1998. Experiments down to 4.2 K are now performed routinely. This instrument also has been incorporated into the teaching curriculum at the University of Kansas with both undergraduate and graduate students learning how to obtain spectra on an EPR spectrometer.

Conclusions: Novel materials have been developed whose electronic properties have been analyzed using a new Bruker 6/1-HX EPR spectrometer that was purchased with this grant. The materials are applicable in gas storage/release processes, chemical sensing, and catalyst development. New methods of material synthesis have been achieved using a modified template copolymerization process. EPR spectroscopy has been integrated into the chemistry curriculum at the University of Kansas.

SIGNIFICANCE: These results show that our method for immobilized metal complexes in porous hosts produces materials that isolate metal centers from each other and thus, can reversibly bind analytes. Materials with the correct architecture have been made to efficiently bind dioxygen under a variety of conditions. NO releasing materials with in vivo activity for the relaxation of smooth muscles have been made. EPR spectroscopy is now used in teaching chemistry students at the University of Kansas

Patent Information: A patent application for the design and fabrication of these new materials has been filed.

PUBLICATIONS AND ABSTRACTS (for total grant period):

- 1 Krebs, J. F.; Borovik, A. S. "Designing Metal Complexes in Porous Organic Hosts", in Molecular and Ionic Recognition with Imprinted Polymers", ACS Symposium Series 703, R. A. Bartsch and M. Maeda, Eds., American Chemical Society, Washington, DC, **1998**, 159-170.
2. Borovik, A. S. (1998). "Designing Metal Complexes in Porous Organic Hosts"; Inorganic Gordon Conference, Newport, RI, . August 1998 (invited talk).
3. Sharma, A. C.; Borovik, A. S. "Design, Synthesis and Characterization of Templated Metal Sites in Porous Organic Hosts: Applications to Reversible Dioxygen Binding," to be submitted.
4. Padden, K.; Krebs, J. F.; MacBeth, C. E.; Borovik, A.S. "The Design, Synthesis and Characterization of an NO Storage/Releasing Polymer: Application to Chemical Sensing, " to be submitted.